# Qualification of new commercial ODS alloys

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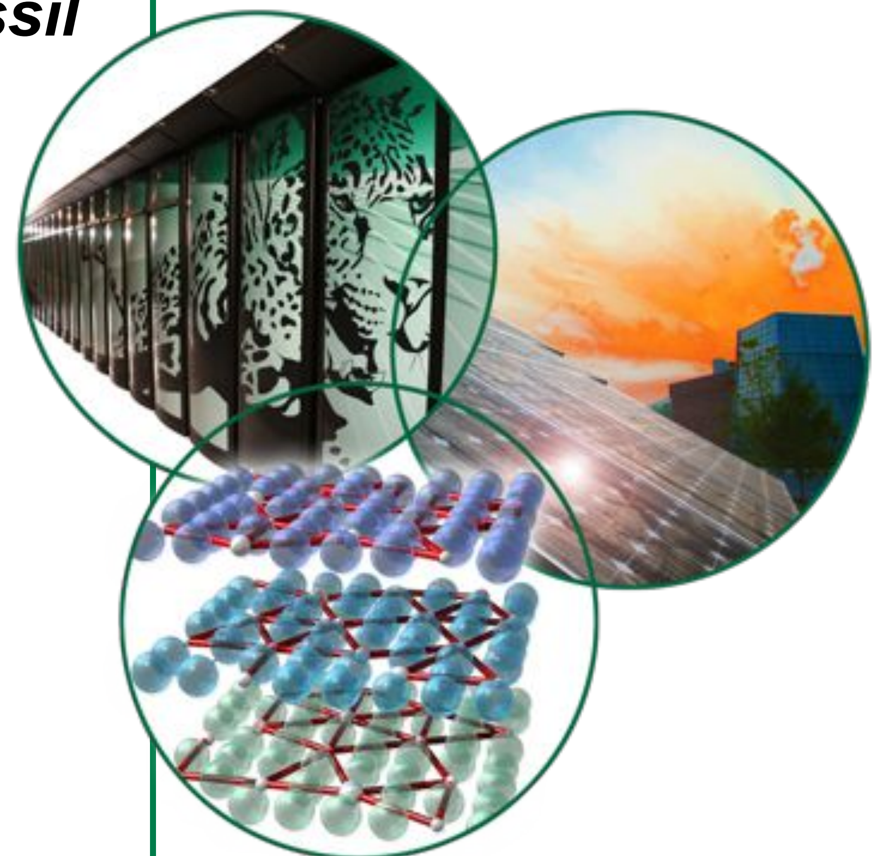

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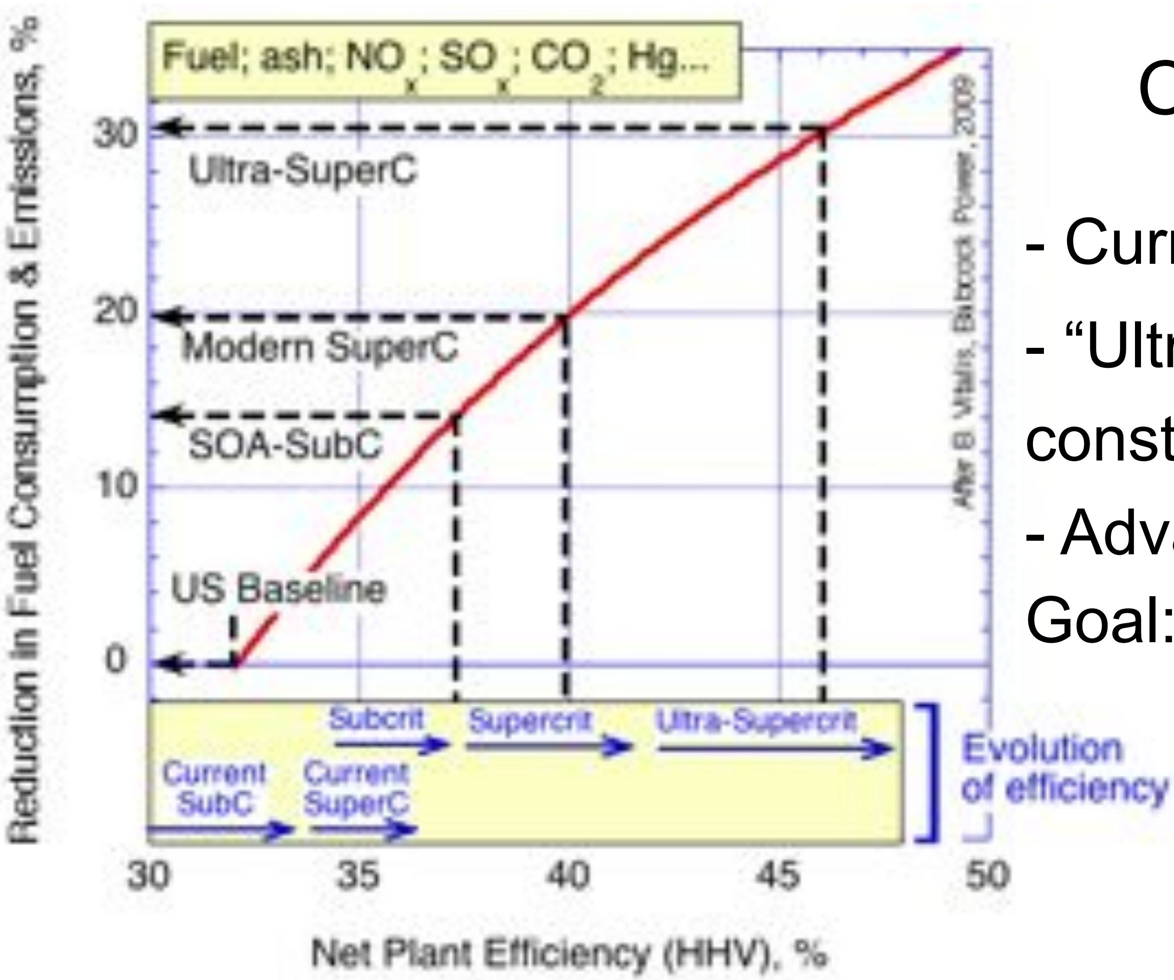
# Increasing the efficiency of power generation system is the goal

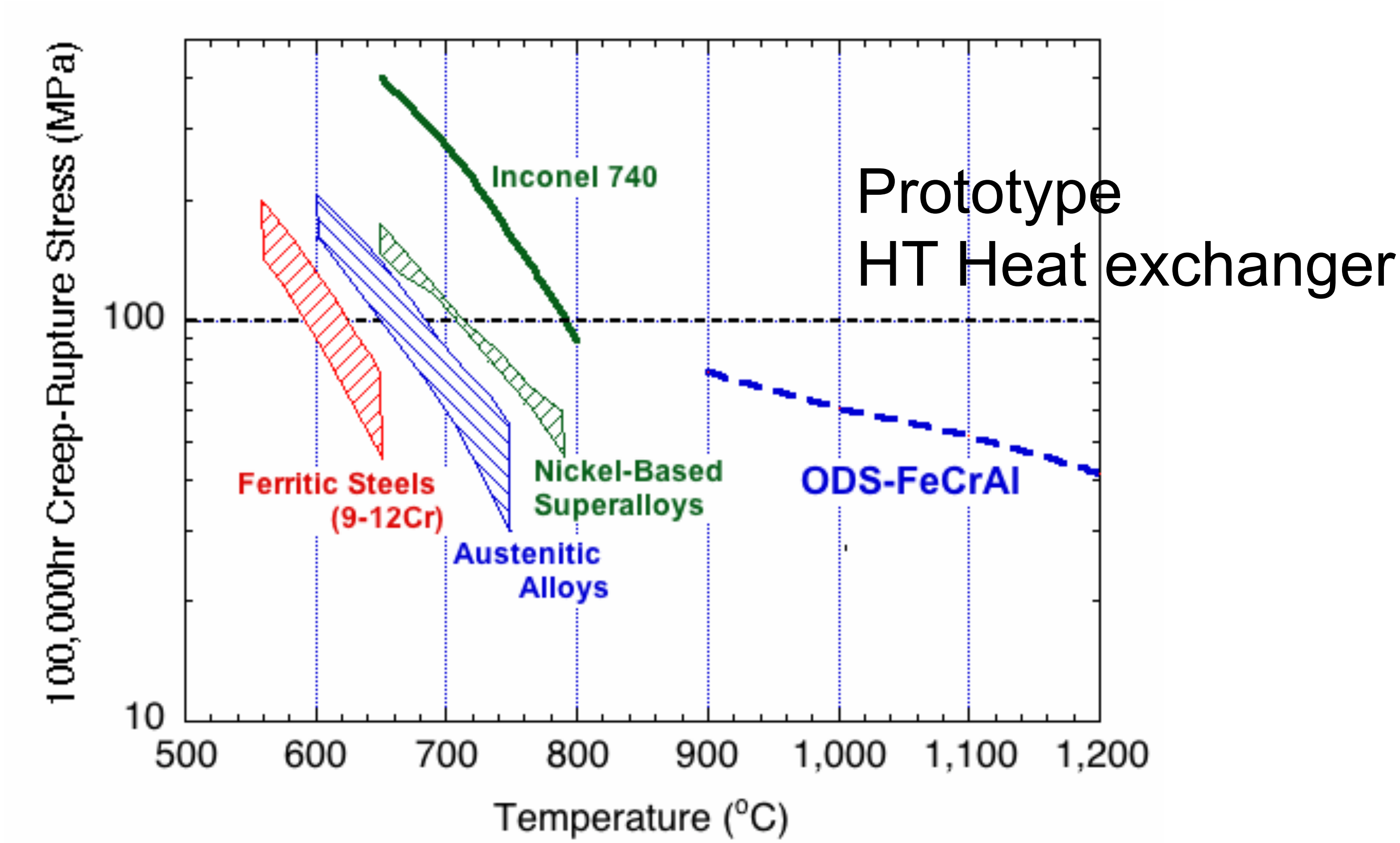



Coal-fired boilers:

- Current fleet average:~550°C
- “Ultra”-supercritical in construction: ~610-620°C
- Advanced Ultra-supercritical Goal: 760°C

# Great potential for high efficiency systems using FeCrAl-ODS alloys

- Oxide Dispersion Strengthened FeCrAl alloys exhibit excellent creep and oxidation properties at T>1200ºC.

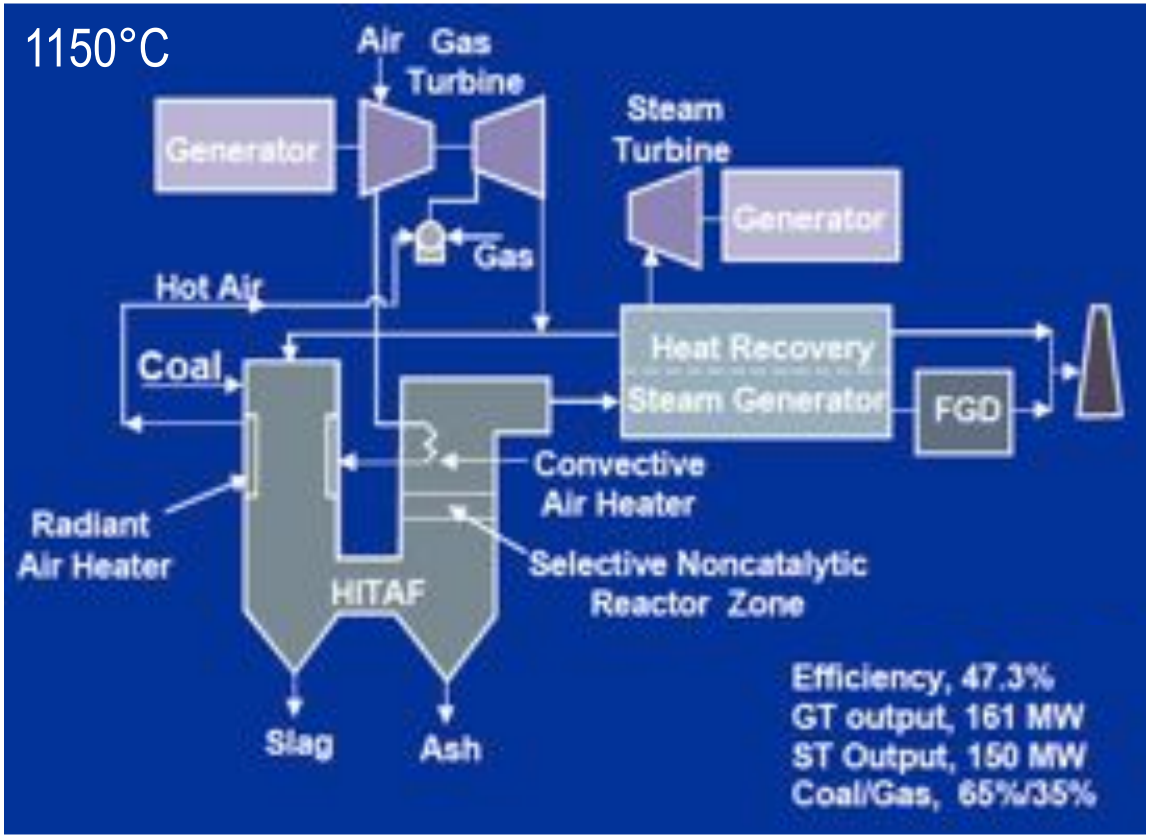


# Power systems with an ODS High Temperature Heat Exchanger

British Gas demonstrator

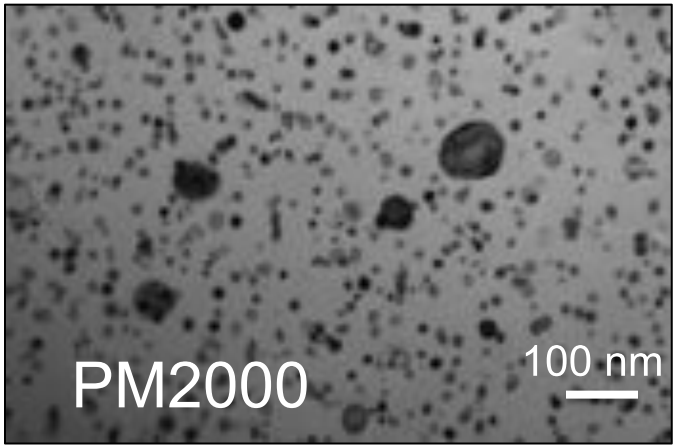

25 mm dia. x 4 m long
ODS FeCrAl Alloy 751

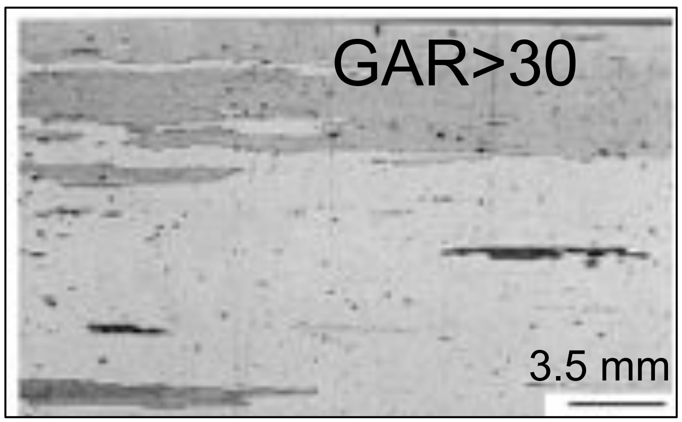
EERC prototype



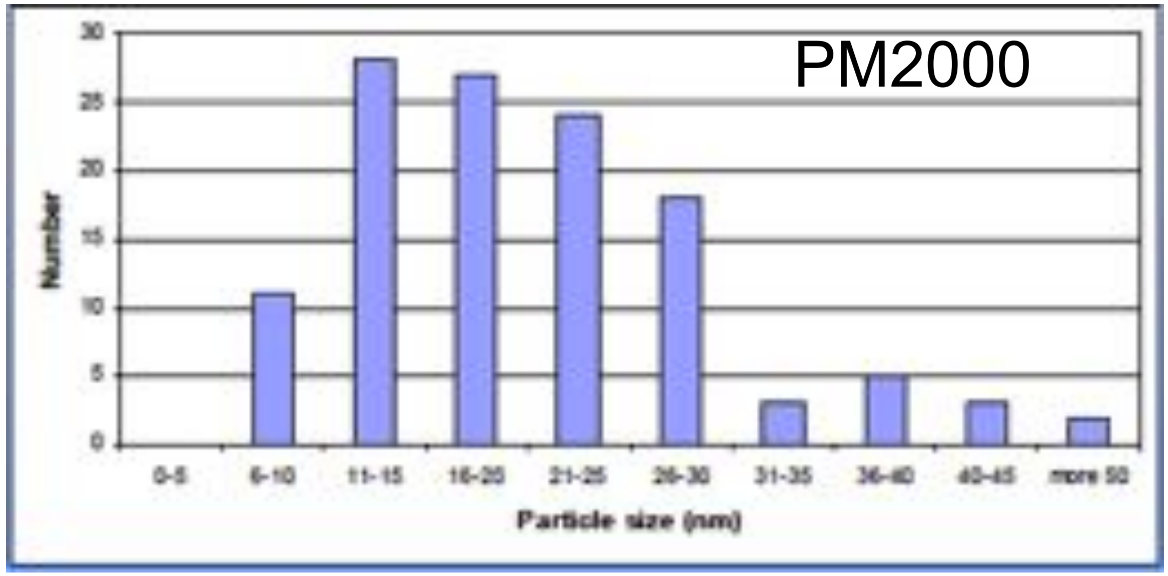

ODS NiCrAl alloy 754 and FeCrAl alloy 956

# FeCrAl ODS alloys microstructure




| | Fe | Cr | Al | Ti | $Y_2O_3$ | Mis. |
|---|---|---|---|---|---|---|
| MA 956 | bal. | 20 | 4.5 | 0.5 | 0.5 | Mo: 1.5 |
| PM 2000 | bal. | 20 | 5 | 0.5 | 0.5 | Mn, Si |
| ODM751 | bal. | 16.5 | 5.5 | 0.6 | 0.5 | Mn, Si |

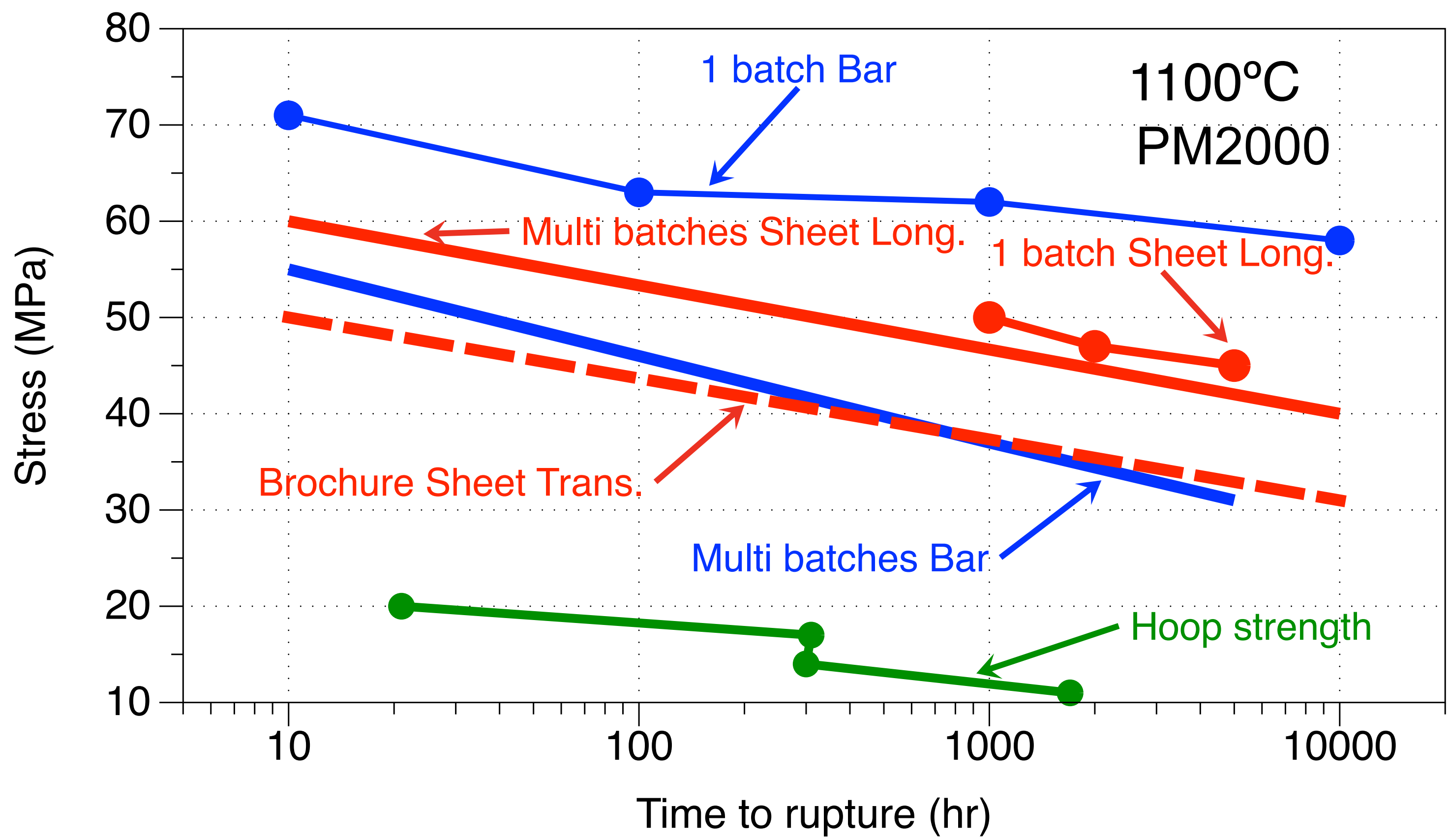



PhD Thesis Laurent Marechal
Capdevila & Al. MSE (2008)

HT creep = nano precipitates obtained by mechanical alloying +
Recrystallisation at HT for large grains

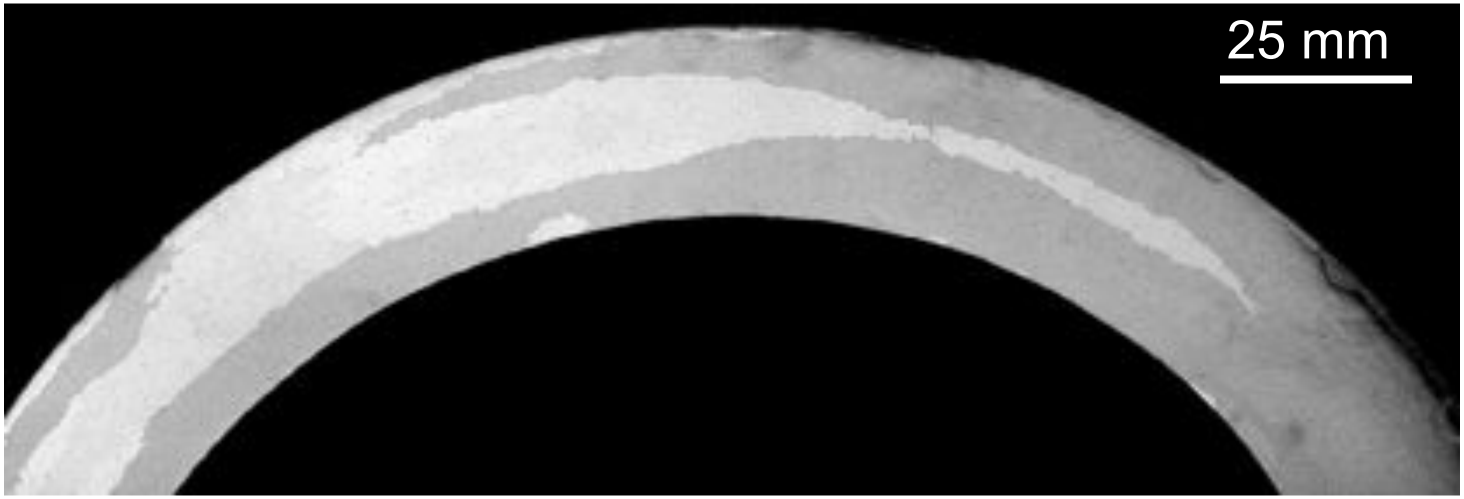
Ex: PM2000: 1h@1380ºC

# Significant variation of creep performance in the literature




-High anisotropy+ Batch process +
very sensitive to fabrication processes

# New supplier: Qualification of a new commercial ODM751 ODS alloys

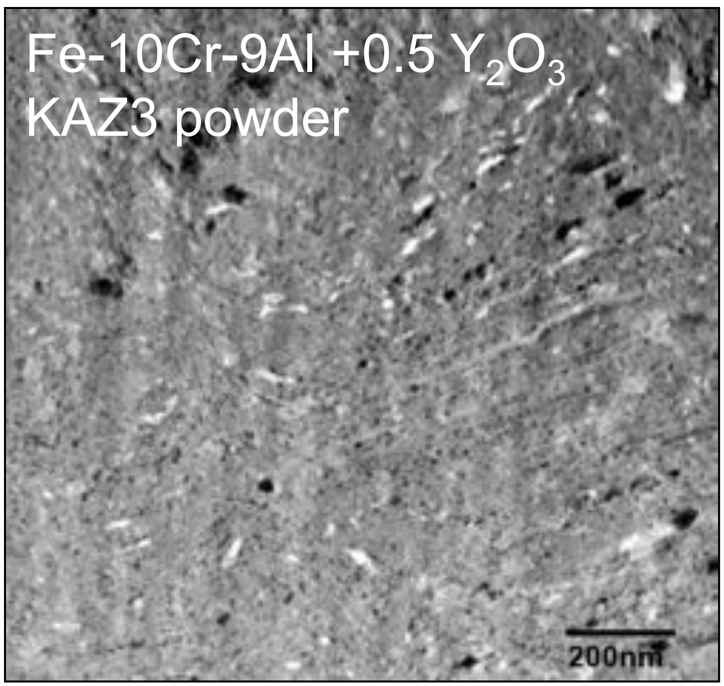


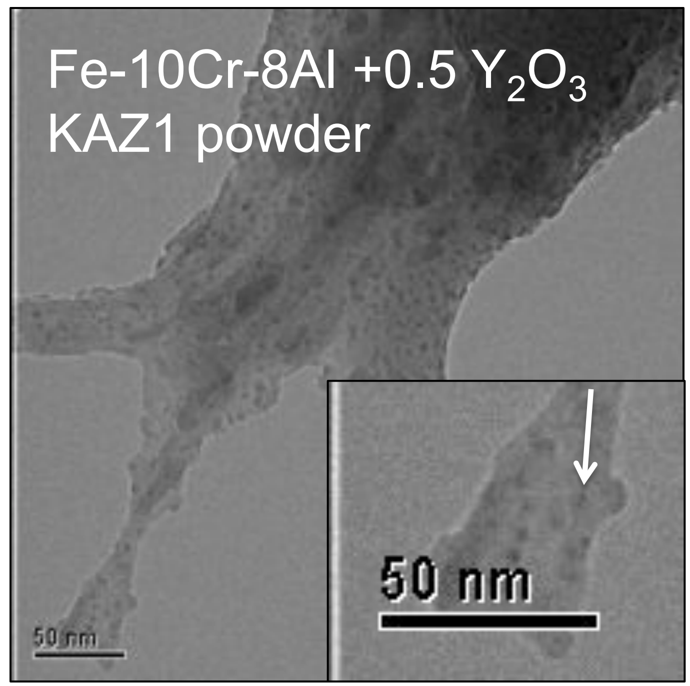

- No commercial ODS alloy supplier: Major concern for end users + new context = high efficiency systems

-Collaboration with Dour Metal Sro. to develop a new commercial ODM751 alloy and fabricate tubes (200kg) with an “onion skin” grain structure with high hoop creep strength

# Characterization of ball milled powder fabricated by Dour Metal

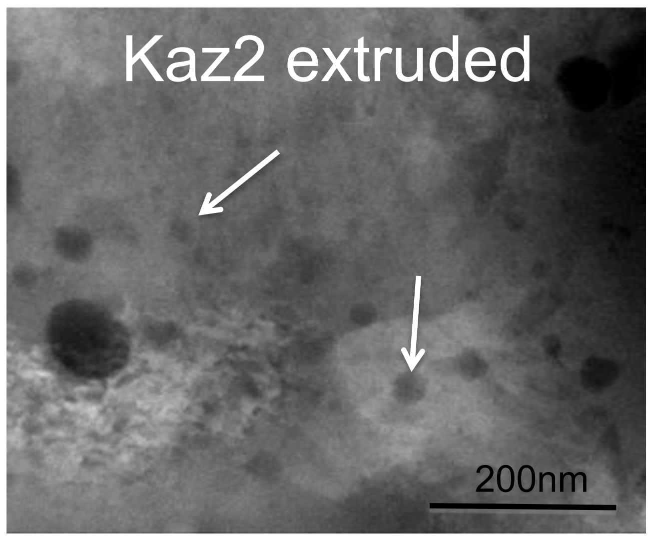
- 3 batches of ODS powder provided by Dour Metal
- Very good powder mixing during ball milling
- Satisfying $Y_2O_3$ precipitates dispersion but many large particles due to impurities level

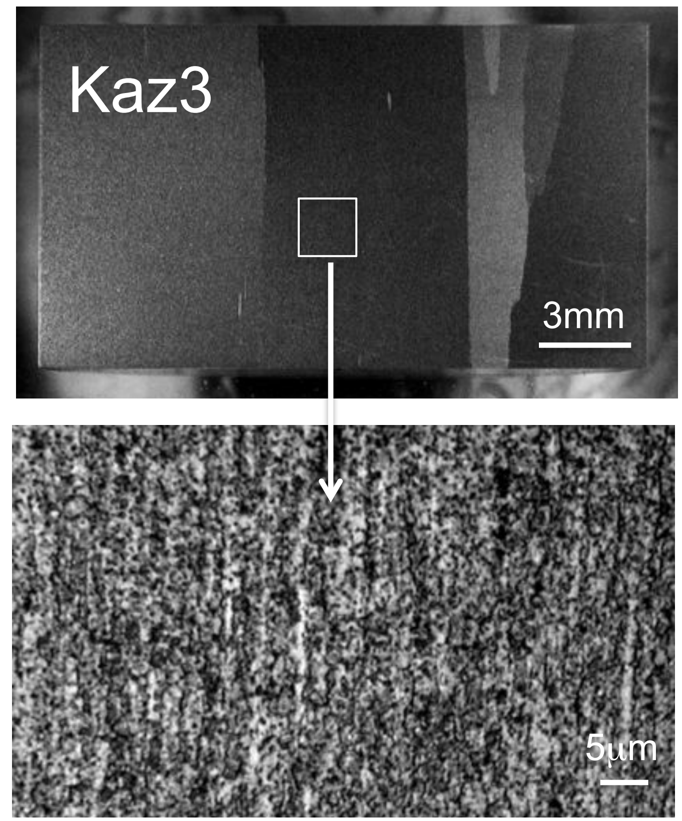


# Extrusion of bars performed at ORNL

- Kaz3 (7kg powder) = bar, 1inch in dia, 6 feet long
- Recrystallisation was not achieved due to high level of impurities

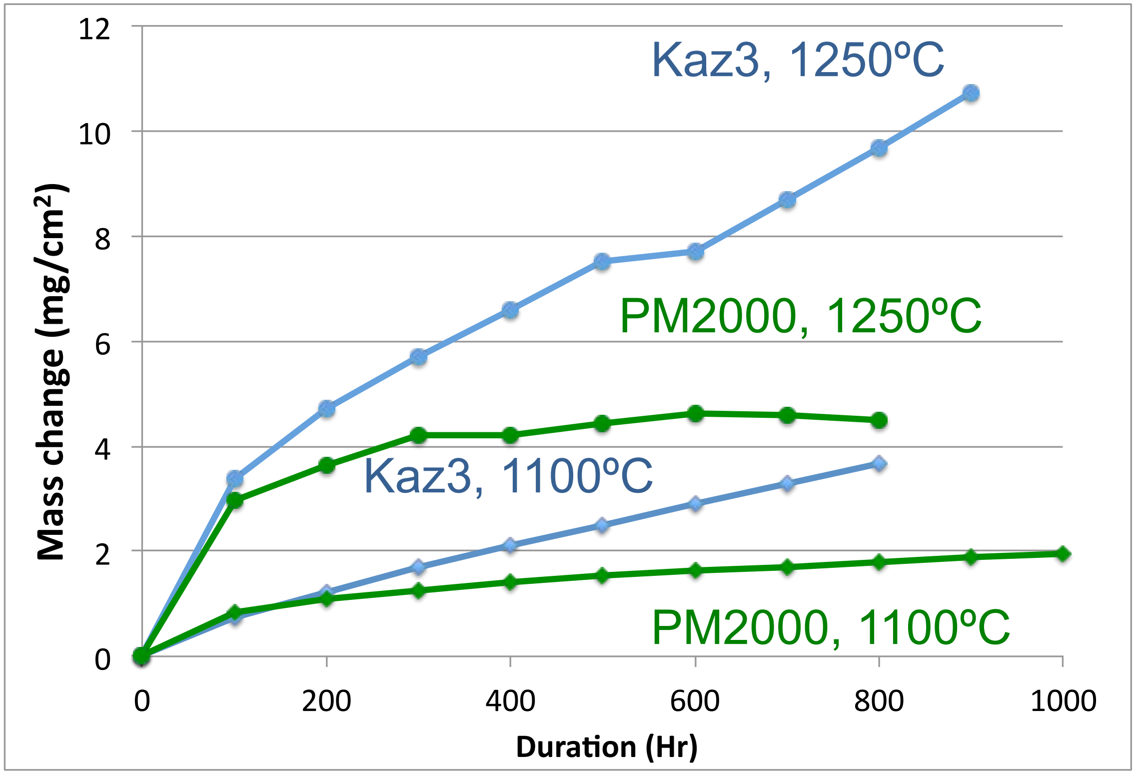



# Basic characterization of Kaz3

- Low creep properties due to high level of impurities

- Oxidation behavior: Kaz3 exhibits higher mass gains than PM2000 but looks like alumina scale formation



# Kaz4: New batch of ODS powder ball milled under low vacuum

- improvement of the ball milling facility to control the environment.

**low impurities content expected**

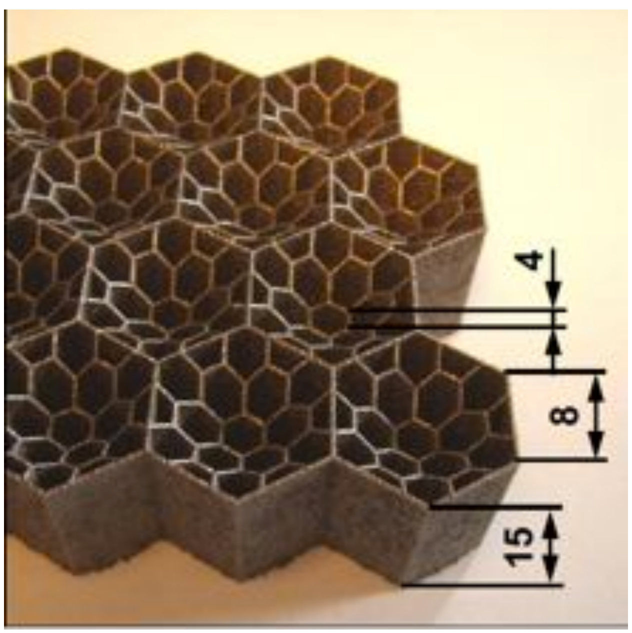
- 2 cans have been Hipped and tubes will be extruded in the coming months

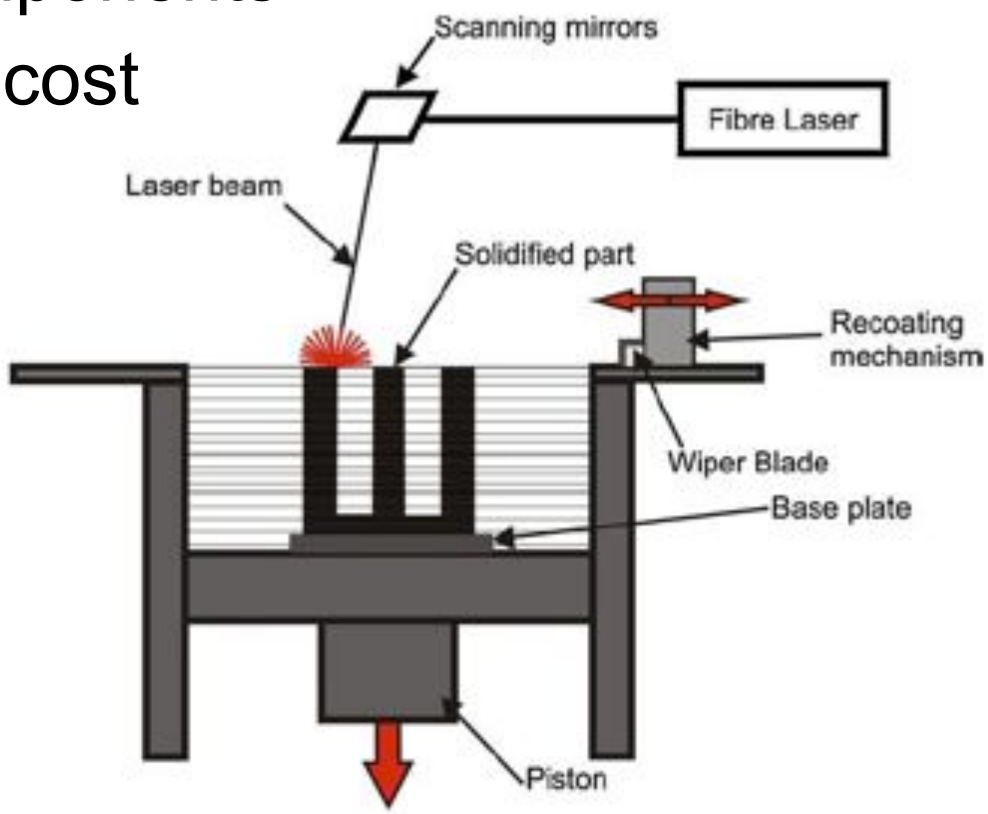
# Selective Laser Melting of ODS alloys

- SLM to apply coatings

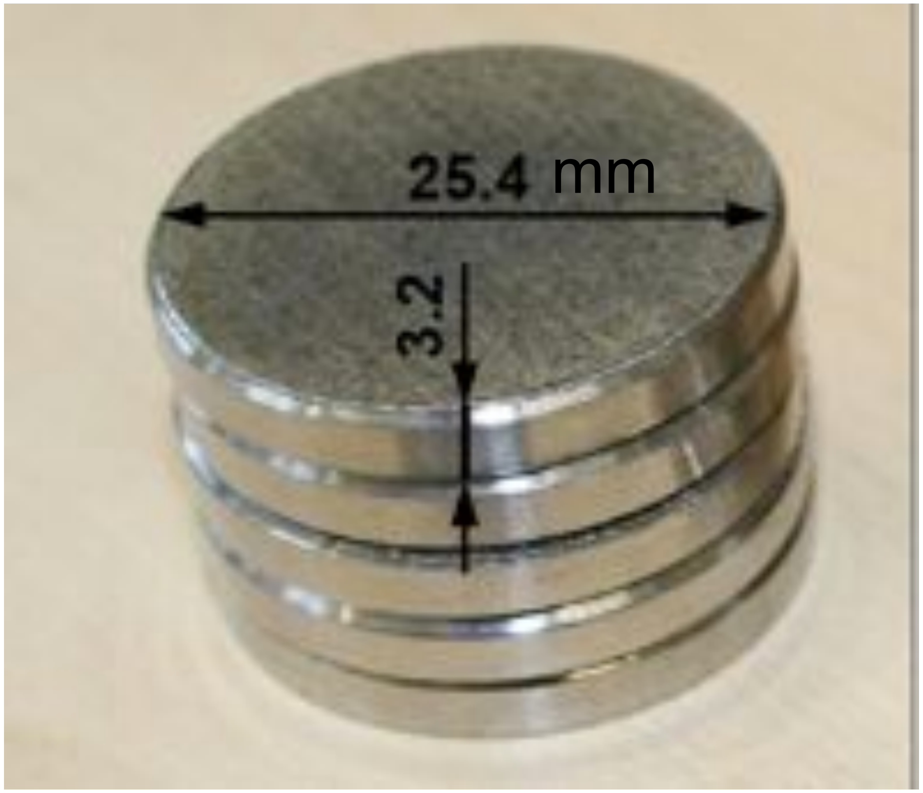
- Rapid prototyping to manufacture near net shape solid components

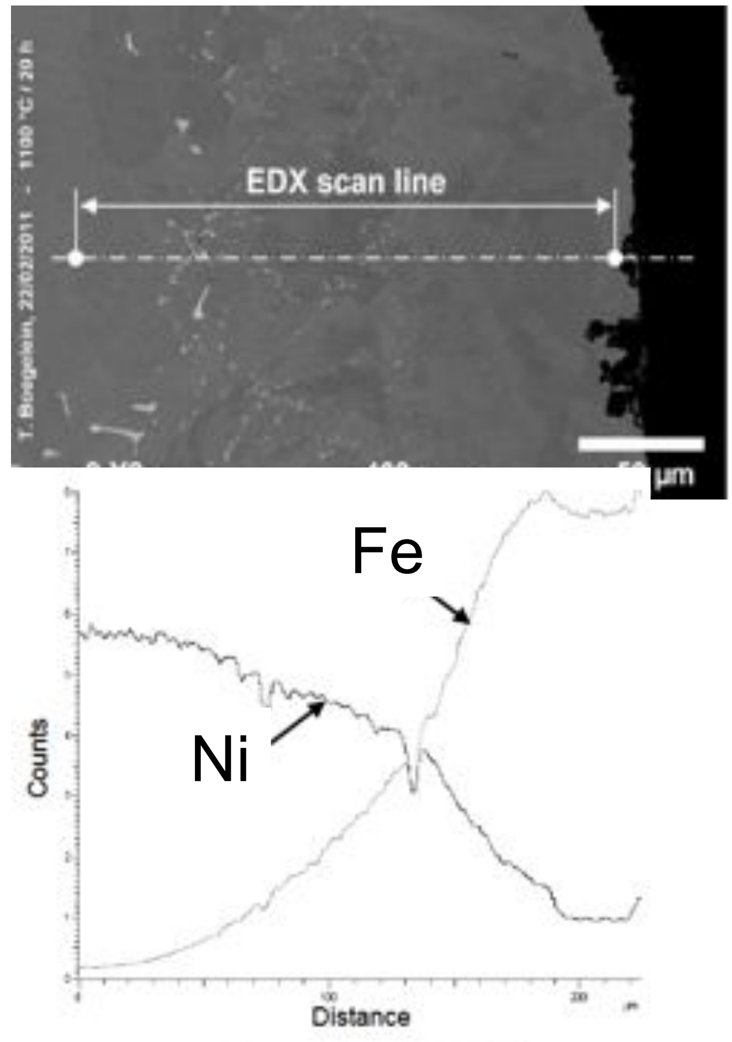
- reduction of fabrication cost



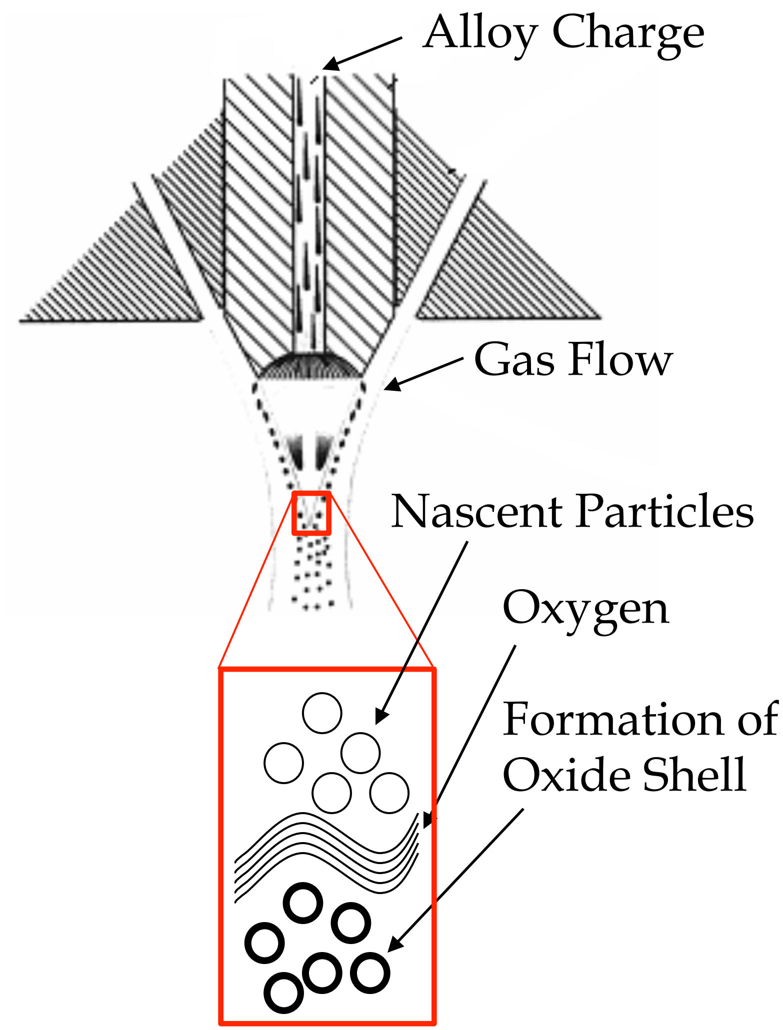
# Effective bond between PM2000 coating and Ni-based IN939 substrate

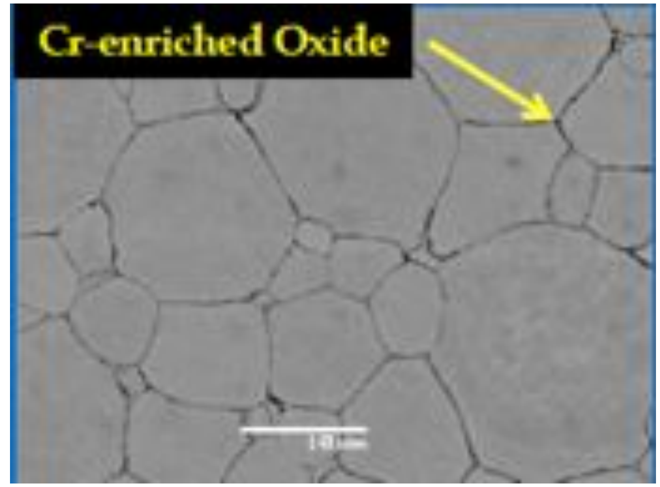



- Characterization of the interdiffusion zone is on-going

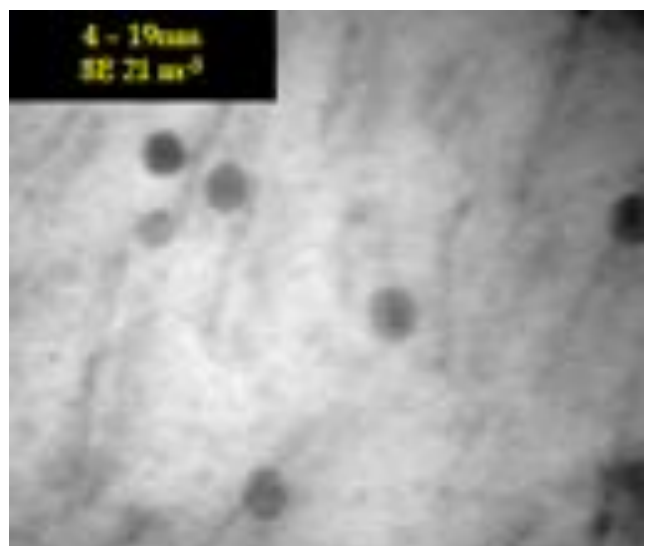
# Gas Atomization Reactive Synthesis to eliminate or decrease ball milling time




HIP 700ºC

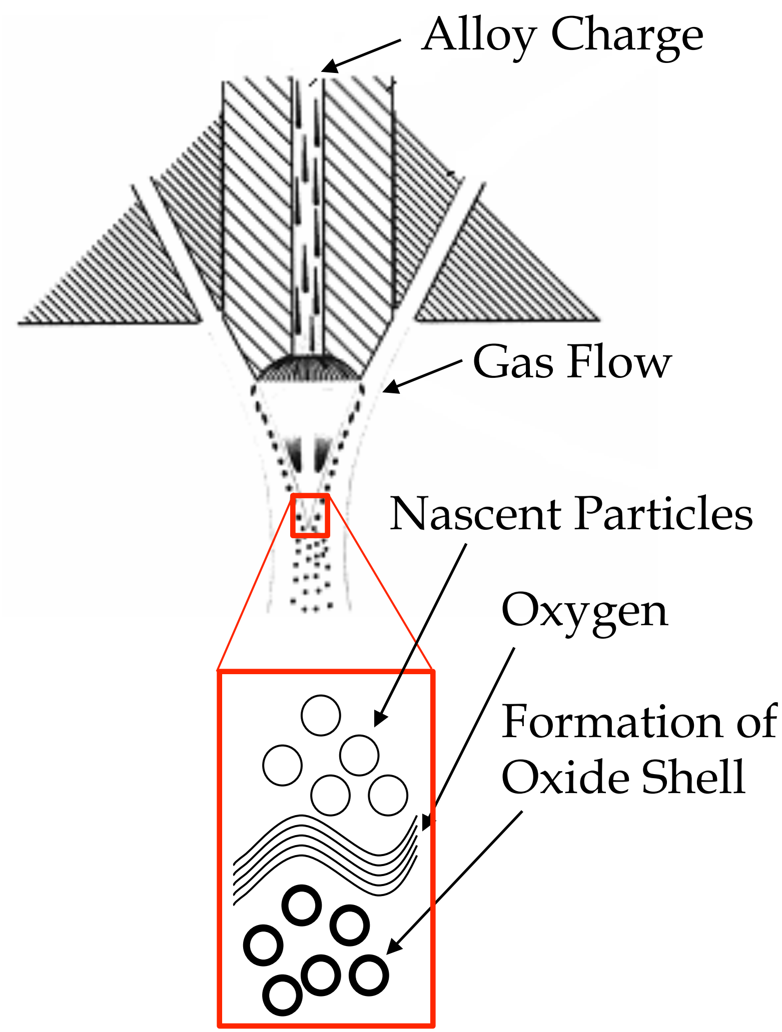
O diffuses and reacts with Y



HT 1200ºC

Ames Lab, I. Anderson, JR Rieken

# Gas Atomization Reactive Synthesis to eliminate or decrease ball milling time




- Consolidation of GARS powder with and without ball milling
- Decrease of ball milling time
  - decrease of cost
  - impurities control
  - continuous process
- Compromise between properties and cost like Sandvik APMT:
  - ideal particle/sieving size?
  - ball milling time?
- incorporation of Al during the ball milling step

# 2010 workshop on the role and future of Fe-based ODS alloys

http://www.netl.doe.gov/publications/proceedings/10/ods/index.html

Objective: to promote end users interest in ODS alloys

Participants: potential users, previous and current suppliers of ODS alloys, component manufacturers and R&D experts

Presentations and discussions focused on:

-ODS alloy availability

- Current state of development of ODS alloys: microstructure, durability (creep, oxidation), weldability

- Past major evaluations of ODS alloys

- Technical and economic issues attendant to wider commercial use of ODS alloys.

# 2010 workshop on the role and future of Fe-based ODS alloys

http://www.netl.doe.gov/publications/proceedings/10/ods/index.html

- Major issues have been discussed: *cost, database, ductility, tailored component application versus straight substitution*…, in light of current state of ODS development

- Suppliers have been approached by potential customers

- Presentations are still available on the website and have been intensively downloaded (586 downloads in March)

**renewed/enhanced interest in ODS alloys**

- Interaction with Nuclear people

# Common Interests / Issues between NE and Fossil

| **Fossil** | **Nuclear** |
| --- | --- |
| Fe20Cr5Al+ $Y_2O_3$ (Ti,Mo) | Fe-9-14Cr+ $Y_2O_3$ (Mo,Ti,W) |

**- Need commercial suppliers**

**- fabrication of cheaper, more reproducible alloys**

| Fossil | | Nuclear |
| --- | --- | --- |
| T°C>900°C<br>Large grain structure | **- Creep resistance** | 900°C>T°C>600°C<br>Nano grain structure |

**- Anisotropic properties due to GAR**

**- Non fusion joining techniques to preserve the ODS structure**

| Fossil | Nuclear |
| --- | --- |
| Oxidation resistance up to 1200°C in aggressive environments ($H_2O$, $CO_2$, $SO_2$…) | Resistance to radiation damage<br>Corrosion resistance (Na…) |

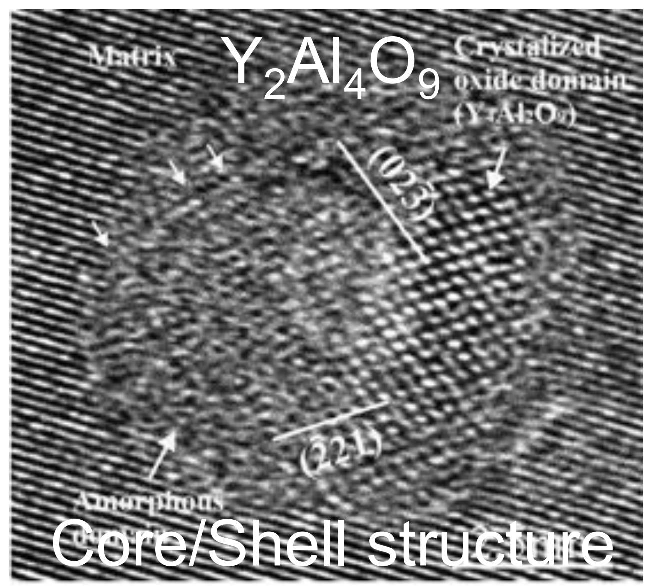
# DIANA I: Workshop on dispersion strengthened steels for advanced nuclear applications

- Development of new FeCrAl ODS alloys with limited thermal ageing embrittlement (475ºC)

K4 (Fe–19Cr–4Al–2W–0.3Ti–0.3$Y_2O_3$)

K3 (Fe–16Cr–4.5Al–2W–0.3Ti–0.37$Y_2O_3$)

- Very high speed planetary milling process
- Reduce impurities level
  - ball milling parameters
  - hydrogen reduction technique
- HR TEM characterization
- Friction stir and resistance welding
- In situ deformation of ODS alloys
- Fracture toughness measurement



# ODS components durability depends on the alloy oxidation resistance

- High temperature creep and oxidation are expected to be the main mode of degradation

- Existence of a stress threshold at a given temperature below which deformation is minimum

- For a mechanically sound component, oxidation will determine the components durability

- Need lifetime models for relevant environments ie containing species such as $H_2O$ and $CO_2$

# Breakaway oxidation is due to Al consumption to form $Al_2O_3$

- $C_b$: critical Al content below which $Al_2O_3$ cannot form
- $C_o$ initial Al concentration
- *FeCrAl models : lifetime = time to drop from $C_o$ to $C_b$*

***Al to form $Al_2O_3$ = Al consumed in the alloy***

$Al_2O_3$

$$S \cdot 1.125 \cdot k \cdot t^n$$

k, n: oxidation parameters

**S: surface**

FeCrAl

$$V \cdot \Delta C$$

$\Delta C = C_b - C_0$

**V: volume**

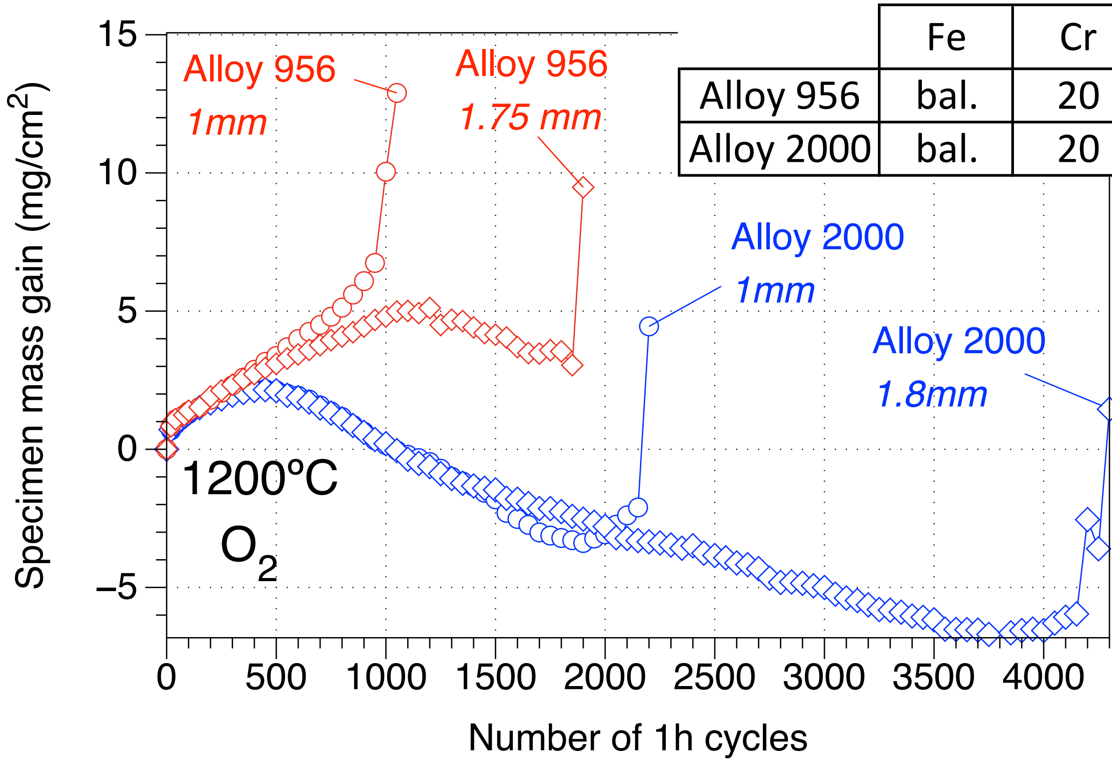
Quaddakers et al. (1994)

$$\boxed{1.125 \cdot k \cdot t_b^n = \frac{\Delta C}{100} \cdot \rho \cdot \frac{d}{2}}$$

**d thickness**

ρ density

# Cyclic oxidation behavior and lifetime of ODS alloys



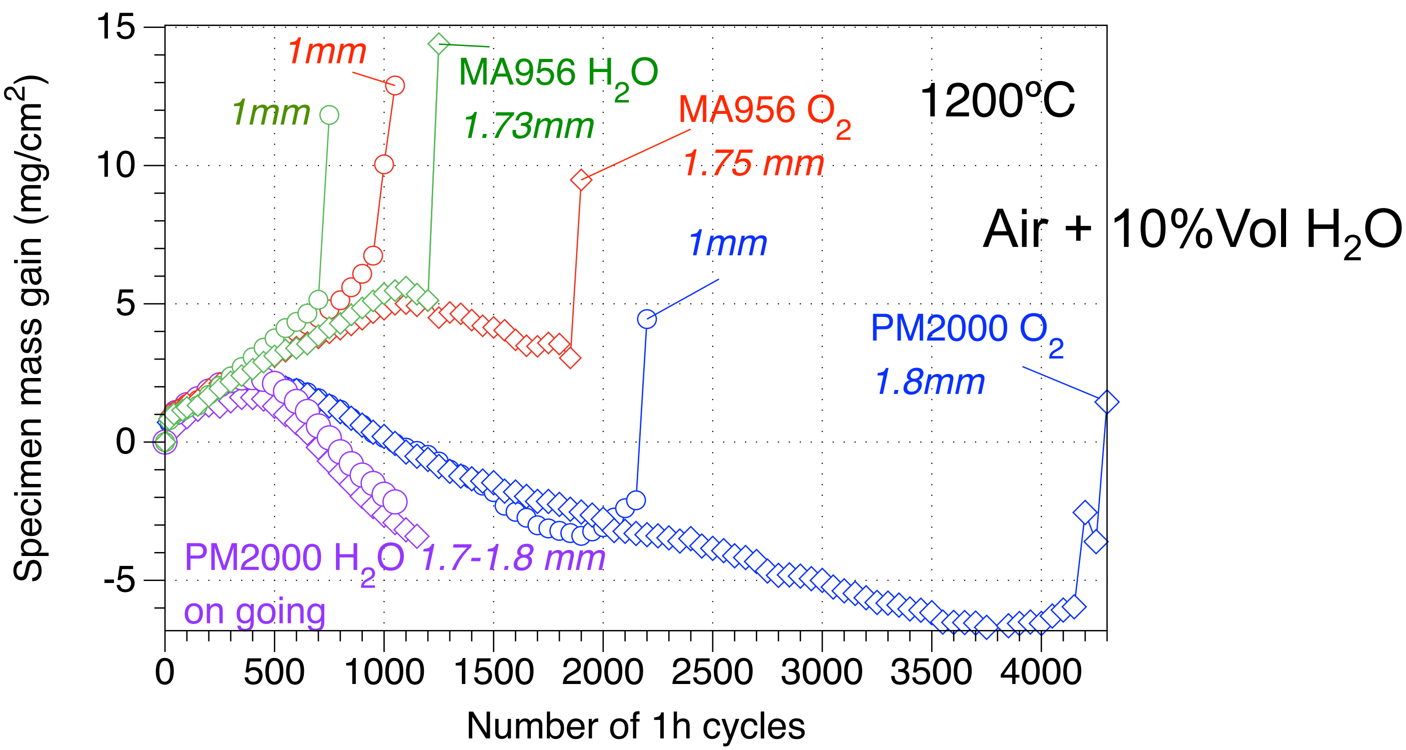

| | Fe | Cr | Al | Ti | $Y_2O_3$ |
|---|---|---|---|---|---|
| Alloy 956 | bal. | 20 | 4.5 | 0.5 | 0.5 |
| Alloy 2000 | bal. | 20 | 5 | 0.5 | 0.5 |

*Low mass change = growth and spallation of $Al_2O_3$*

*Breakaway oxidation = fast formation of Fe-rich oxides*

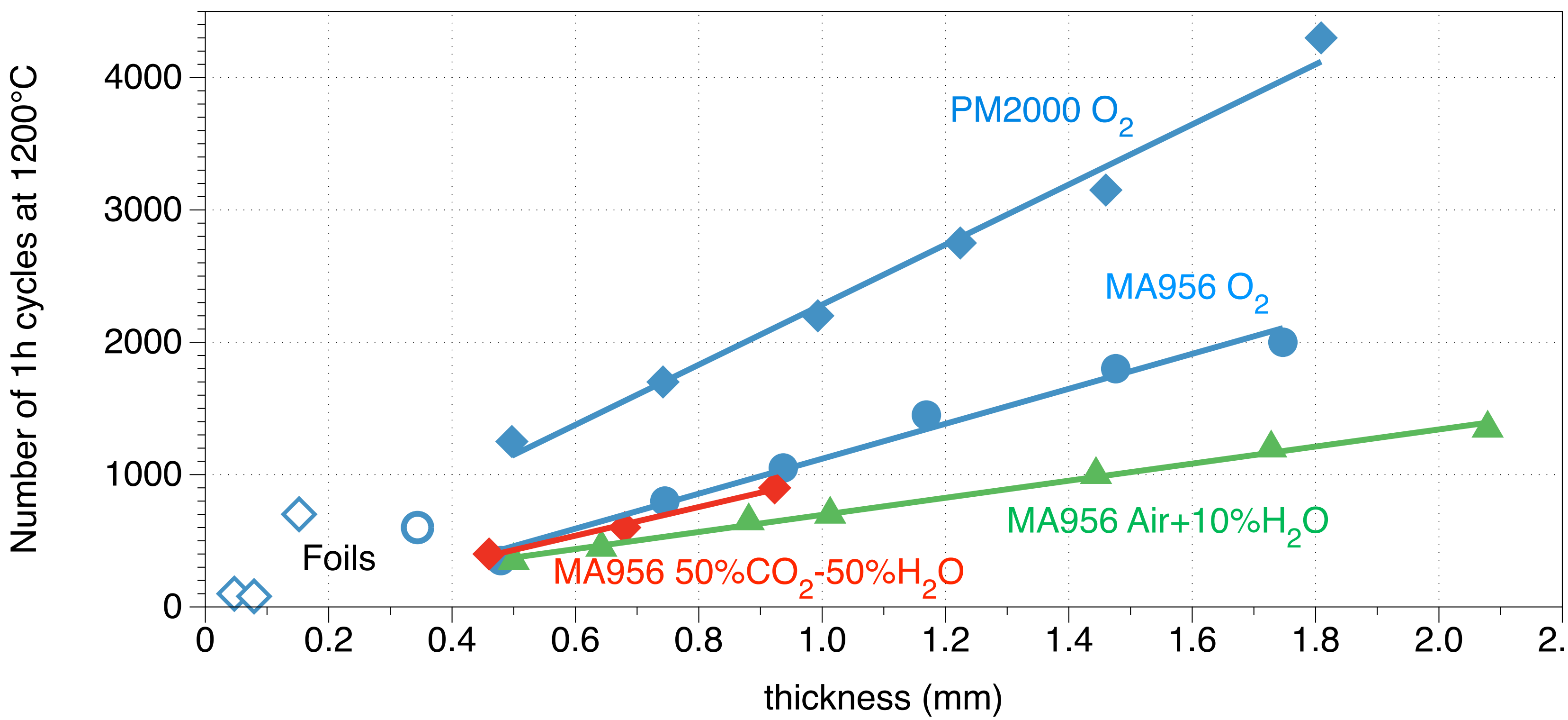
≈ end of life

# Significant effect of $H_2O$ on mass gain curves




- Decrease of time to rupture for MA956
- Change in oxidation kinetics for PM2000

# Significant effect of $H_2O$ on lifetime
# Slight effect of $H_2O/CO_2$




Linear relationship between lifetime and thickness for all the specimens

Significant decrease in lifetime in $H_2O$

# Breakaway oxidation is due to Al consumption to form $Al_2O_3$

- $C_b$: critical Al content below which $Al_2O_3$ cannot form
- $C_o$ initial Al concentration
- *FeCrAl models : lifetime = time to drop from $C_o$ to $C_b$*

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$$S \cdot 1.125 \cdot k \cdot t^n$$

k, n: oxidation parameters

**S: surface**

FeCrAl

$$V \cdot \Delta C$$

$\Delta C = C_b - C_0$

**V: volume**

Quaddakers et al. (1994)

$$\boxed{1.125 \cdot k \cdot t_b^n = \frac{\Delta C}{100} \cdot \rho \cdot \frac{d}{2}}$$

**d thickness**

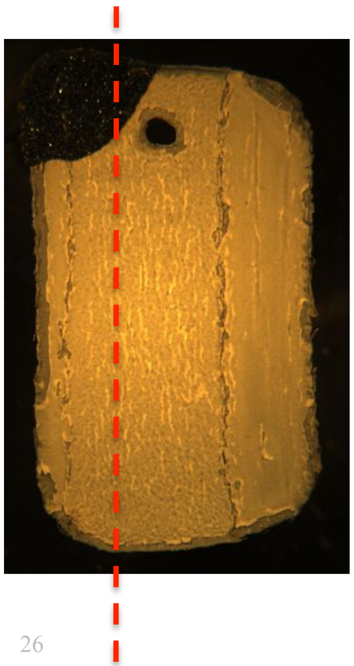
ρ density

# How Al is consumed in the alloy?

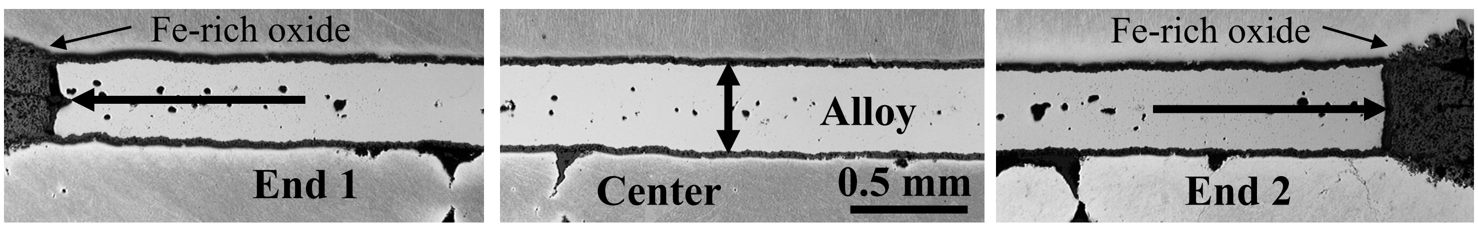
$$1.125 \cdot k \cdot t_b^n = \boxed{\frac{C_b - C_0}{100} \cdot \rho \cdot \frac{d}{2}}$$

What is $C_b$? Uniform consumption of Al?

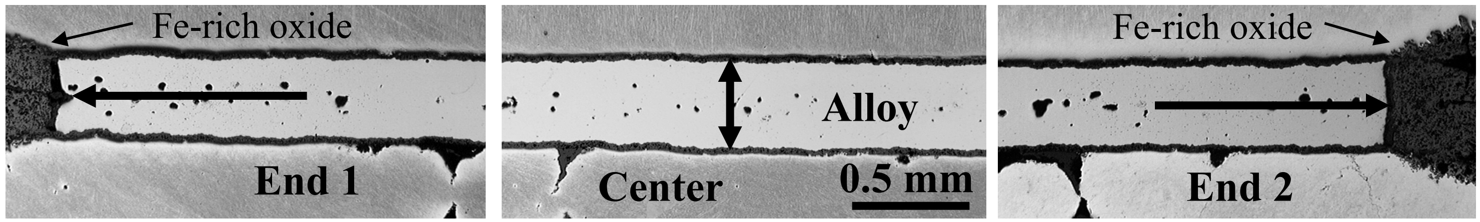
What about Al gradients from the specimen center to the surface?
How does $C_b$ change with T, cycles…

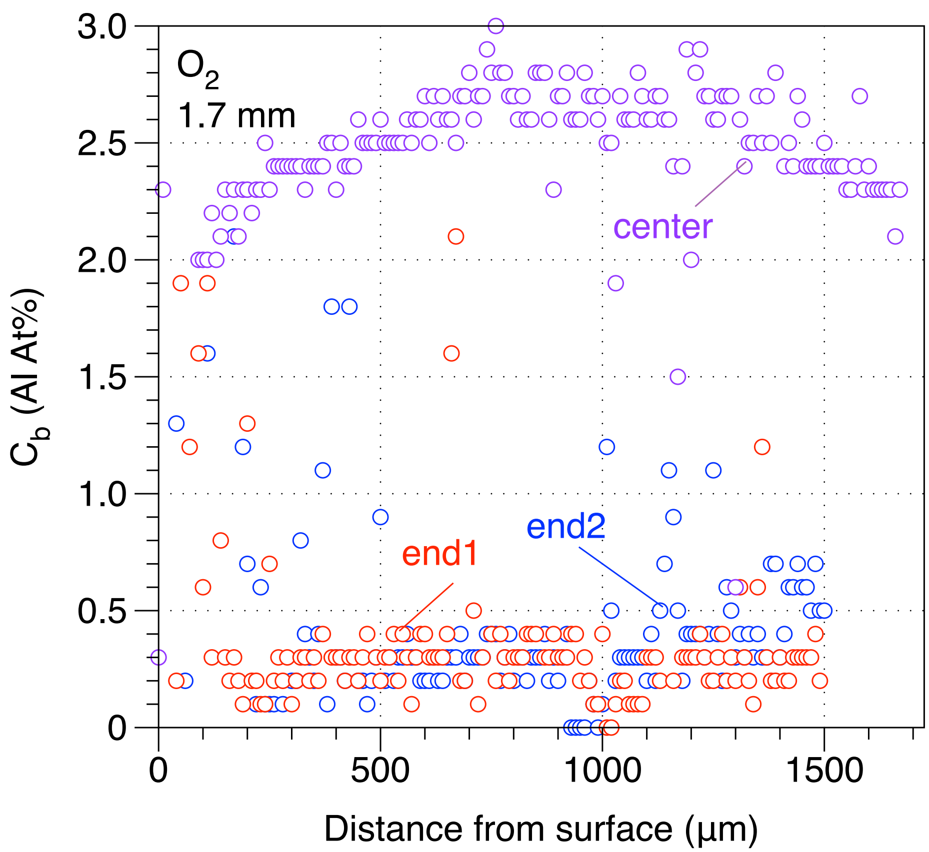


Microprobe profile to determine Al remaining after the onset of breakaway oxidation



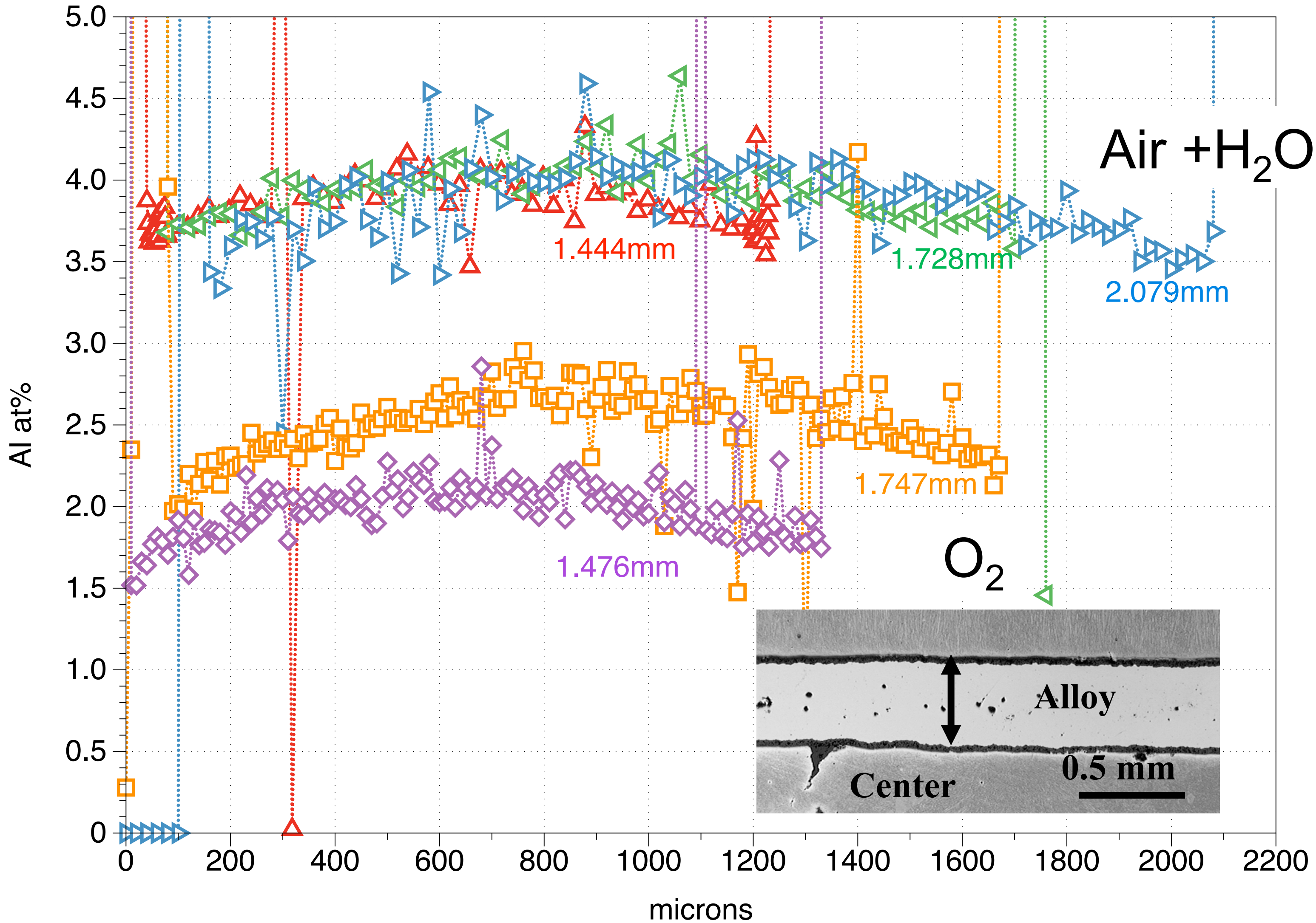
# Measurement of the remaining Al content



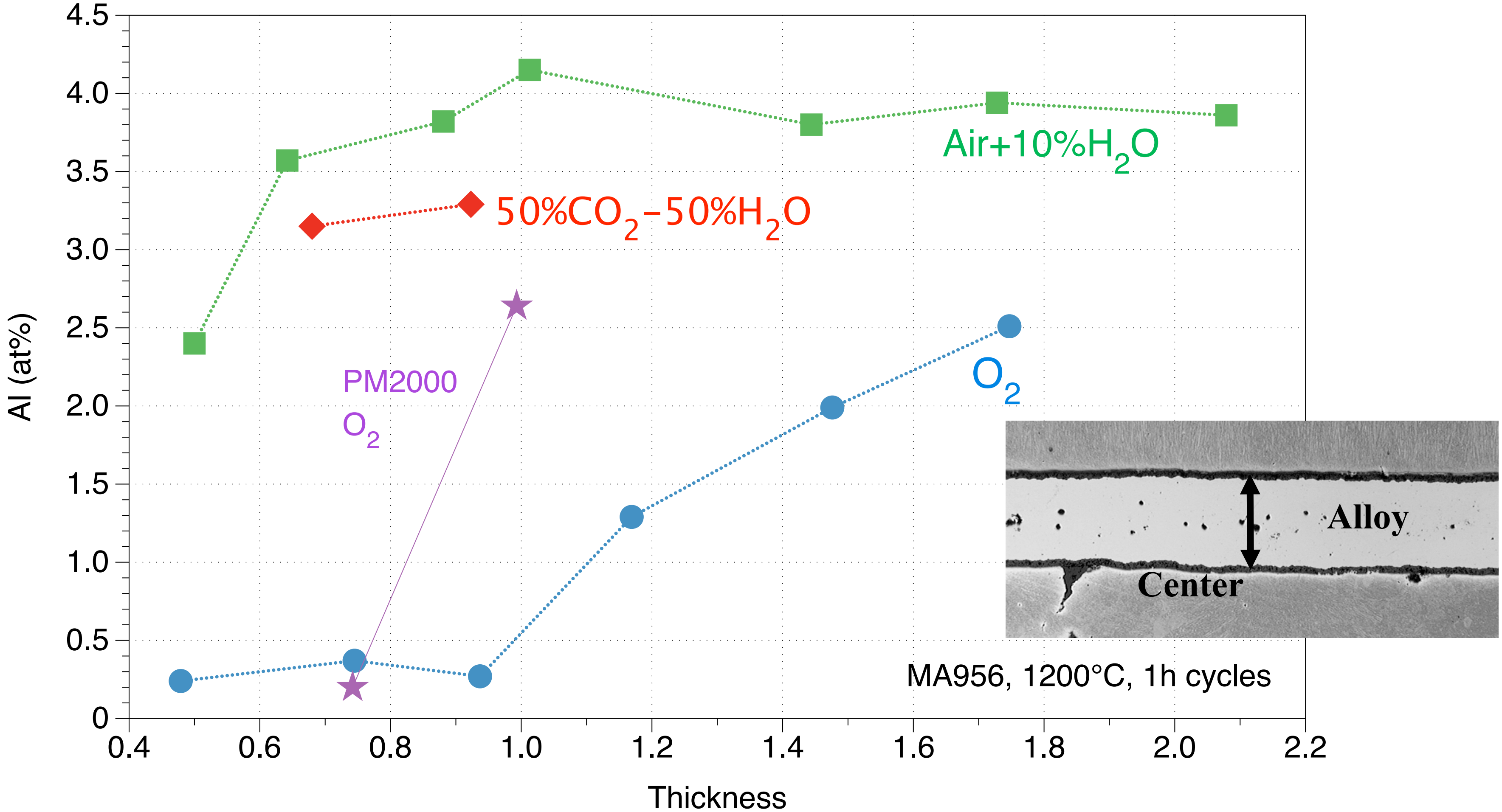




- Significant difference in Al content at the ends and in the center of the specimen
- What matters? concentration at the center or at the edge?

# Effect of $H_2O$ on Al consumption

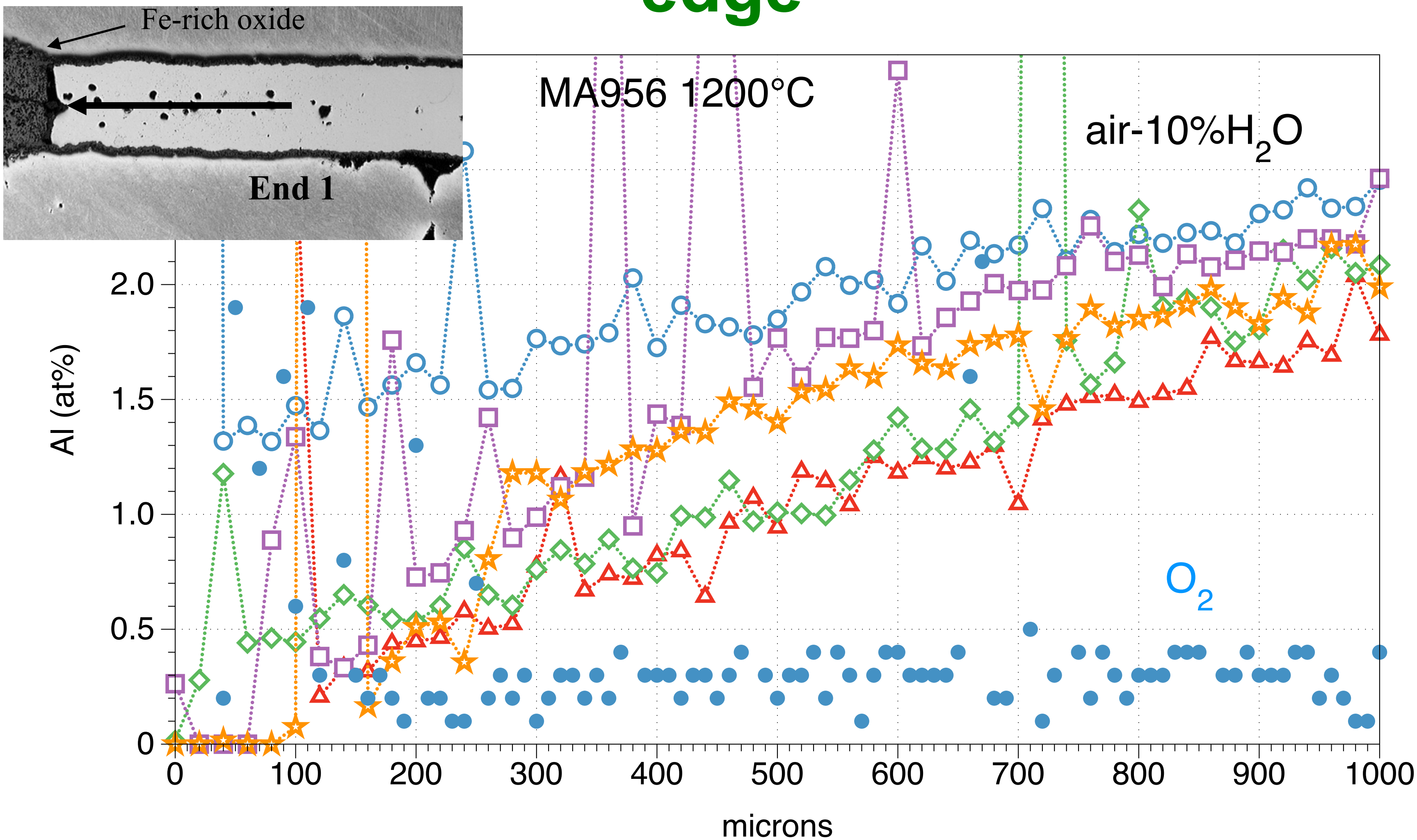


# Effect of thickness and environment on Al concentration at the specimen center



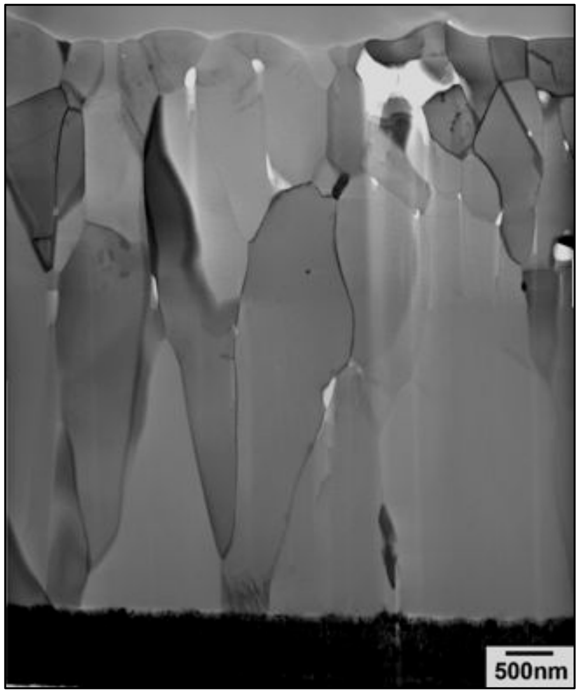

Optimization of the Al reservoir?

# Significant Al gradient in air + $H_2O$ at the edge

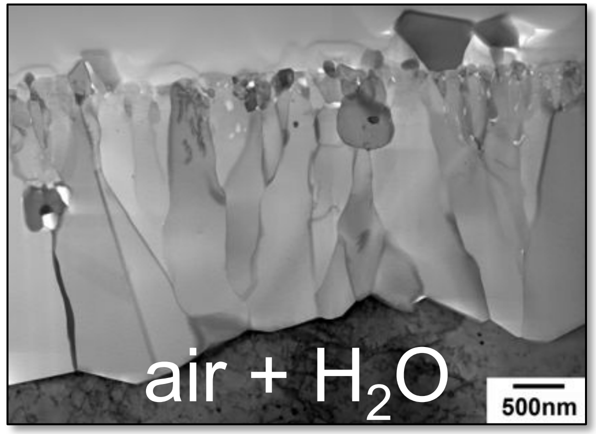


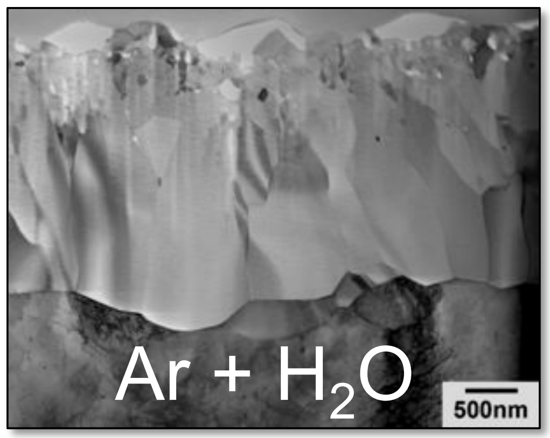

Lower lifetime with $H_2O$ because of Al diffusion change in the alloy?

# Isothermal oxidation, 500hr at 1100ºC
# Thinner oxide scale with $H_2O$




$O_2$



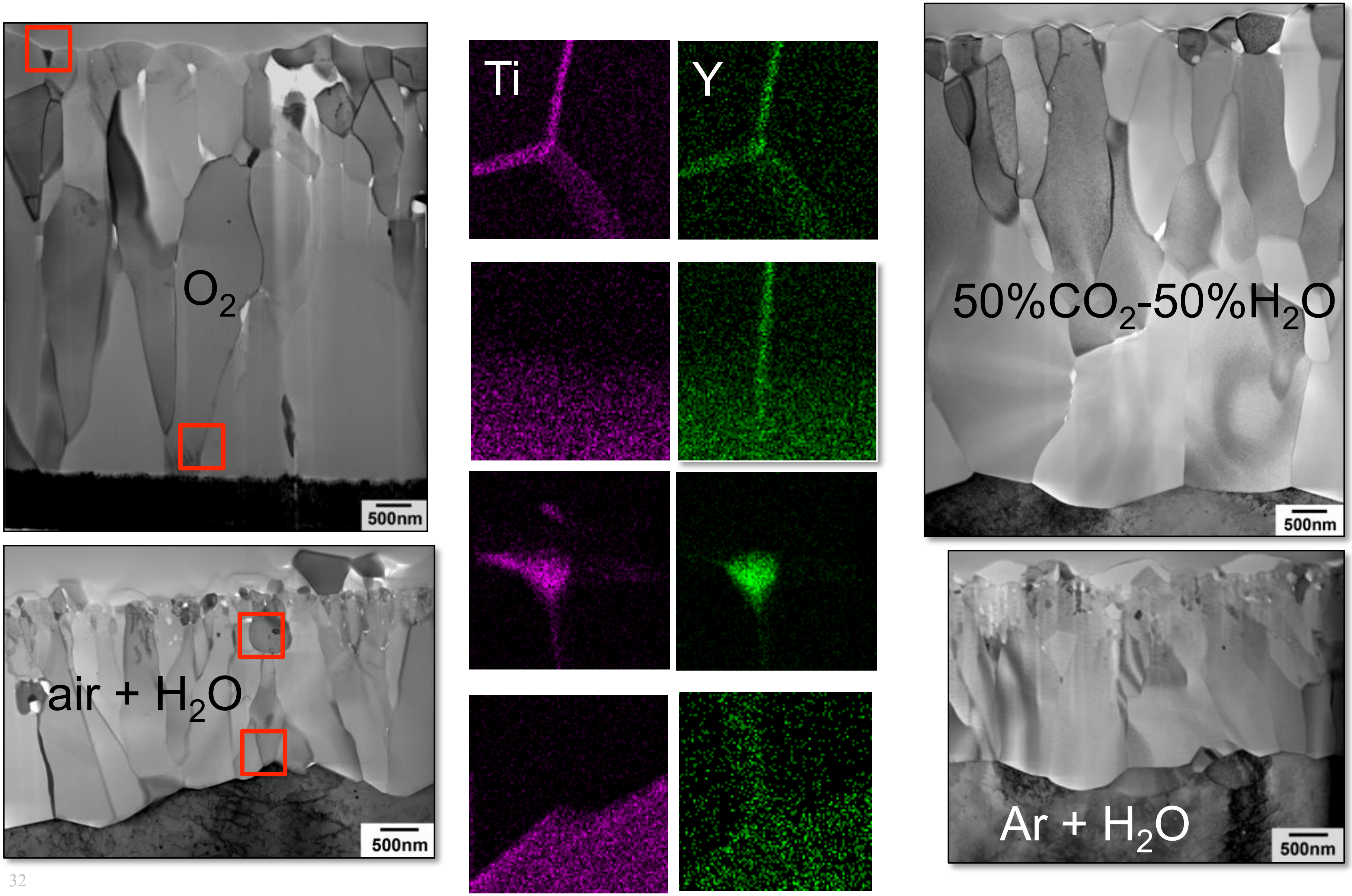





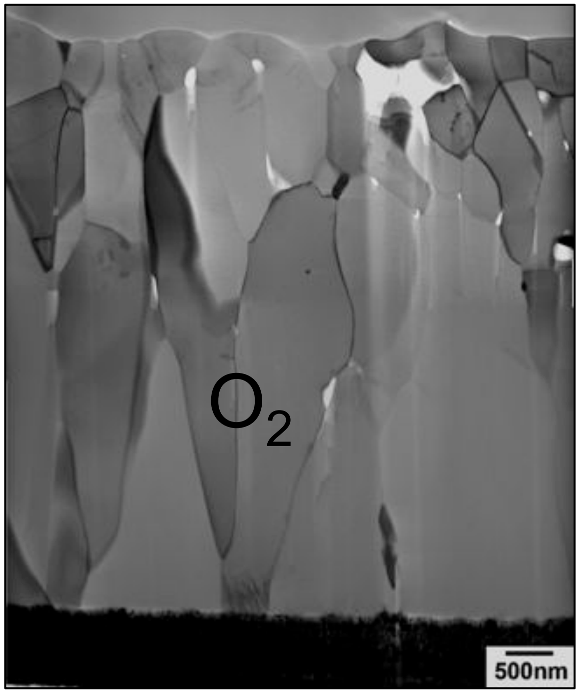
50%$CO_2$-50%$H_2O$

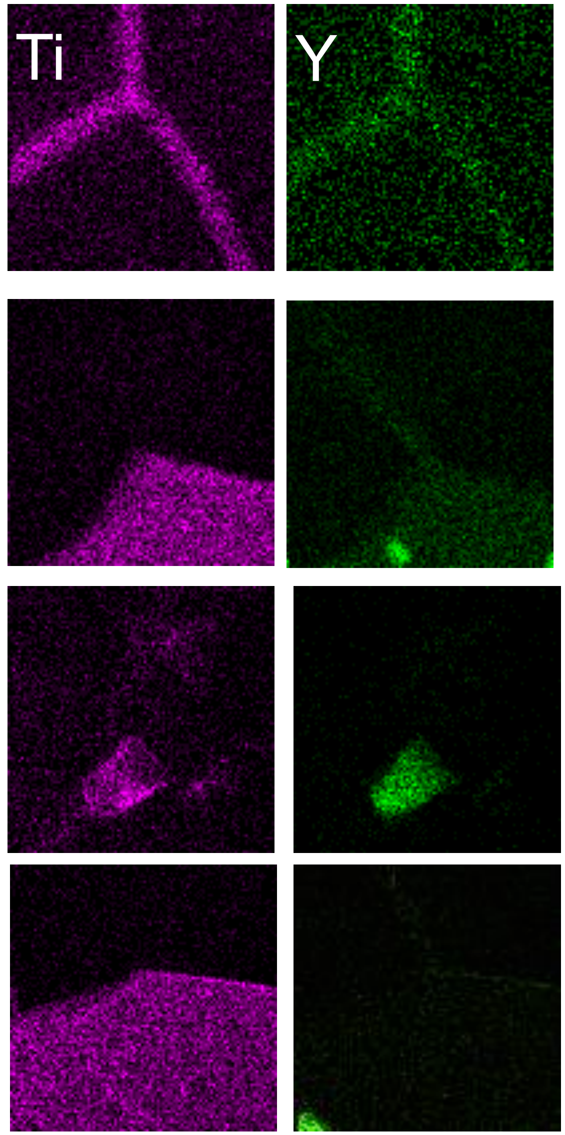
Different diffusion species through alumina? ($OH^-$, $H_2O$)
Different trend in comparison with 1h 1200ºC testing

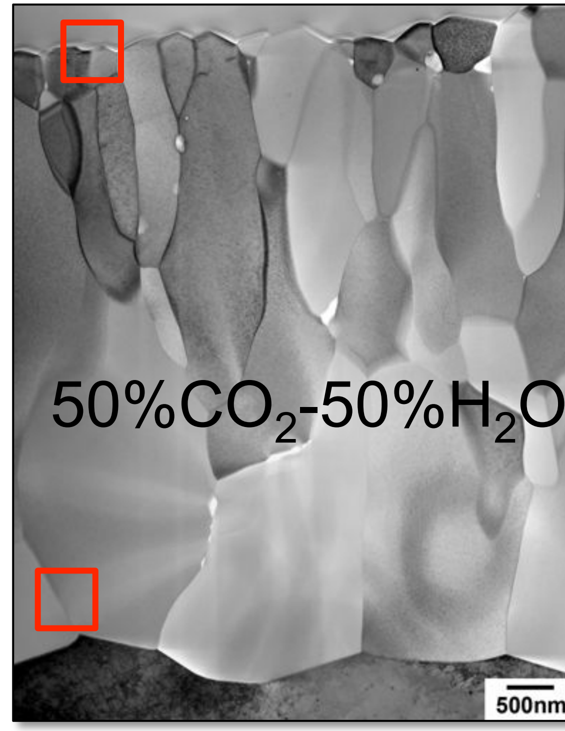
# Ti and Y at GB interface. Only Y at metal interface

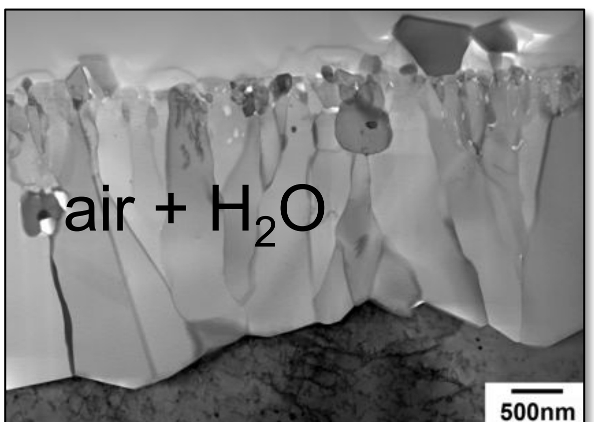


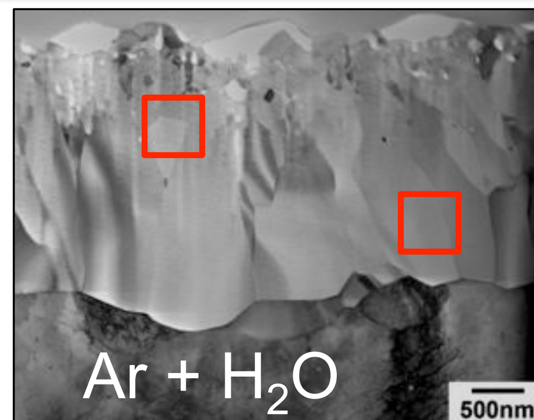
# Understanding segregation is key to a very protective alumina scale



# Conclusions

- Tubes of ODM751alloy with low level of impurities and an onion skin grain structure will be extruded in the coming months
- Different approaches are under consideration to lower the cost of ODS components
- ODS workshop was successful in boosting interest for ODS alloys

*More information: Google: "ODS workshop 2010"*

- Work is on going to improve the understanding of ODS alloys oxidation in complex environments ($H_2O$, $CO_2$…) and improve lifetime models
- Need a better understanding of creep deformation and rupture at high temperature

# Acknowledgements

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- All the workshop participants
- G. Garner, T. Brummett, Mike Howell, L. Hu and L. Walker for assistance with the experimental work
- B. Pint, I. Wright and E. Essuman for exiting scientific discussions
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